



Electrochemical investigation of carbonate-based electrolytes for high voltage lithium-ion cells[☆]

Libo Hu, Zhengcheng Zhang*, Khalil Amine

Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA

HIGHLIGHTS

- Conventional carbonate-based electrolytes are investigated in LNMO cells.
- Cell performance is optimal when charged to 4.8 V followed by a CV charging step.
- Carbonate-based electrolytes decompose readily above 4.9 V.
- Cell performance degrades dramatically at high temperature.
- The decomposition of carbonate electrolytes is more severe on the cathode.

ARTICLE INFO

Article history:

Received 20 November 2012

Received in revised form

9 January 2013

Accepted 22 February 2013

Available online 4 March 2013

Keywords:

Carbonate-based electrolyte

High voltage cell

5 V LiNi_{0.5}Mn_{1.5}O₄ cathode

Electrochemical performance

Lithium-ion batteries

ABSTRACT

One conventional electrolyte ("Gen 2") for lithium-ion batteries consists of 1.2 M LiPF₆ dissolved in ethylene carbonate and ethyl methyl carbonate. A comprehensive investigation of this electrolyte in a high-voltage graphite/LiNi_{0.5}Mn_{1.5}O₄ (LNMO) cell was carried out to evaluate its voltage stability under various charging conditions. Although the carbonate-based electrolyte was relatively stable when the graphite/LNMO cell was charged to 4.8 V at room temperature, the introduction of a constant-voltage charging step aggravated the oxidative decomposition of the electrolyte. Further increase in the cell charging voltage to 4.9 V or above and further increase in the temperature to 55 °C caused cell performance to deteriorate dramatically.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

As one of the most used batteries in consumer portable electronics in recent decades, lithium-ion technology has been gaining increasing popularity and is moving toward high energy high power applications, such as hybrid and plug-in electric vehicles [1,2]. The most efficient way to raise the energy and power density of a battery pack is to increase the capacity and the voltage of individual

cells. As a result, high-voltage cathode materials such as LiNi_{0.5}Mn_{1.5}O₄ (LNMO) and LiCoPO₄ have been developed to raise the cell voltage from the 3.7 V in cells with LiCoO₂ cathode material up to 5 V [3,4]. However, the increased voltage limit of the cathode materials poses challenges to the development of high-voltage stable electrolytes used in such cells. The voltage stability of the conventional electrolytes is well studied [5–7] with inert electrodes such as Pt or glassy carbon. The voltage limits vs. Li/Li⁺ of the carbonate electrolytes are usually reported above 5 V, suggesting the possibility of application in a high voltage cell.

However, due to the highly catalytic nature of the cathode materials, the actual voltage limits of the electrolyte are usually much lower than those obtained with an inert electrode. Lucht and coworkers [8] reported that an EC/DMC/DEC-based electrolyte starts to show considerable decomposition with the LNMO cathode when the cell is charged over 4.5 V vs. Li/Li⁺. Other studies have also been carried out to improve the performance of the conventional EC-based electrolyte by using additives [9]. However,

[☆] The submitted manuscript has been created by UChicago Argonne, LLC, Operator of Argonne National Laboratory ("Argonne"). Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract No. DE-AC02-06CH11357. The U.S. Government retains for itself, and others acting on its behalf, a paid-up nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

* Corresponding author. Tel.: +1 630 252 7868; fax: +1 630 972 4440.

E-mail address: zhang@anl.gov (Z. Zhang).

to our knowledge, no thorough study has been conducted to evaluate how the EC-based electrolyte performs in a high voltage cell, how the charging conditions affect the performance of the EC-based electrolyte, and whether increased temperature also affects the performance. For this reason, it is extremely important to establish a performance baseline for conventional electrolytes, so that future research on either additives to improve the existing electrolytes or new stable electrolytes to improve the high voltage performance can have a well-defined starting point as a reference. To realize this goal, we report a comprehensive investigation of the electrochemical performance of the EC/EMC-based electrolyte in the graphite/LNMO electrochemical couple under a variety of testing conditions.

2. Experimental

An electrolyte of 1.2 M LiPF₆ dissolved in EC/EMC (3:7 in weight), designated as Gen 2 electrolyte [10], was purchased from Tomiyama Pure Chemical Industries, Ltd., and was used as received.

The leakage current at various voltage of the electrolytes to determine the voltage stability were conducted in a 20 mL glass vial with a 2-mm-diameter disk platinum electrode as the working electrode and lithium foil as the reference and counter electrodes. The experimental apparatus was setup in an inert glove box filled with argon with a cable connected outside to a Solartron 1470E Cell Test System electrochemical analyzer (current resolution 1.5 nA).

The graphite anode used a laminate composition of 89.8 wt % of Conoco Phillips CGP-A12, 4 wt% Super P–Li, 6 wt% Kureha 9300 PVDF binder and 0.2 wt% oxalic acid coated on copper foil. The vacuum oven dried anode measures 50 microns thick, with the copper foil measures 10 microns and the coating measures 40 microns. The loading averaged 5.3 mg cm⁻². The LNMO cathode used a laminate composition of 84 wt% LiNi_{0.5}Mn_{1.5}O₄ powder, 8 wt % Super P–Li and 8 wt% Solyve 5130 PVDF binder coated on aluminum foil. The vacuum oven dried cathode measures 92 microns thick, with the aluminum foil measures 20 microns and the coating measures 72 microns. The loading averaged 12.5 mg cm⁻².

The charge–discharge cycling performance with the EC/EMC-based electrolyte was determined with 2032 coin cells having LNMO as the cathode, graphite as the anode, and microporous polyethylene/polypropylene/polyethylene as the separator. The effective electrode area was 1.6 cm². Results were recorded by a Maccor Electrochemical Analyzer. For the graphite/LNMO cells, a two-cycle formation was performed with a rate of C/10 between 3.5 and 4.9 V, and then the cell was cycled at designated charging/discharging voltages (usually between 3.5 and 4.9 V unless otherwise specified), C-rates (usually C/3 unless otherwise specified), and temperatures (usually at RT or 55 °C) and analyzed by the software associated with the Maccor Electrochemical Analyzer (MIMSClient). Also tested were Li/graphite and Li/LNMO half cells. For the Li/graphite, two formation cycles were performed at a rate of C/15 between 1.5 and 0.01 V. For the Li/LNMO, one formation cycle was performed at room temperature at a rate of C/10 between 3.5 and 4.95 V.

3. Results and discussion

3.1. Anodic stability study

Although the anodic stability of the EC-based electrolytes has been studied [5–7], the reported values are quite scattered due to the lack of a uniform evaluation method and experimental conditions. In these papers, cyclic voltammetry was employed to define the anodic potential limit. As reported by our recent publication [10], we have employed a new method that measures the leakage

current over time of an electrolyte under a constant-potential electrolysis process. The current intensity reflects (1) the electrochemical instability due to decomposition at a given potential and (2) the anodic potential limit of the electrolyte, as indicated by a sudden jump of the leakage current. Fig. 1 summarizes such tests on the Gen 2 electrolyte using the Pt/Li/Li electrochemical cell at room temperature.

The results show that the Gen 2 electrolyte has negligible leakage current at voltages up to 5.4 V vs. Li/Li⁺. The electrolyte starts to show moderate decomposition at 5.5 V and intense decomposition over 5.9 V. These findings suggest that the Gen 2 electrolyte should be a good candidate for the high-voltage cell with spinel cathode (5.0 V). However, due to the catalytically active metal-oxide cathode surface, decomposition actually tends to start at much lower potentials. This test using an inert electrode serves only as a reference for stability studies of new electrolytes; however, the voltage stability observed in the test correlates well with the cell performance using a Li₄Ti₅O₁₂ anode, as we reported [11].

Fig. 2 shows the differential capacity profiles (dQ/dV) of the first cycle of Gen 2 electrolyte in Li/graphite and Li/LNMO half cells. The Li/graphite half cell shows typical EC-based electrolyte characteristics, as evidenced by the peak associated with solid–electrolyte interface formation at around 0.6 V vs. Li/Li⁺. In contrast, the Li/LNMO did not show any additional peaks until the delithiation of the cathode material. However, the absence of peaks unrelated to delithiation does not necessarily indicate electrolyte stability or passivation on the cathode surface. It is speculated that electrolyte decomposition occurs during the delithiation process, and the indicative peaks are buried in the major dQ/dV peaks. By using X-ray photon spectroscopy (XPS) and Fourier transform infrared (FT-IR) spectroscopy, Lucht and coworkers found that the EC/DMC/DEC-based electrolyte decomposes at 4.5 V vs. Li/Li⁺, and they proposed that the polymerization of EC may occur on the cathode surface due to an increased intensity of the signal for carbonyl functional group [8].

3.2. Capacity retention at normal charging condition 3.5–4.9 V

The Gen 2 graphite/LNMO full cell was operated for 100 cycles at room temperature (RT) and 55 °C to compare the degree of decomposition, as shown in Fig. 3. The full cells were charged to 4.9 V with constant current (CC) charging at 0.67 mA, approximately C/3, and then were constant-voltage charged at 4.9 V for

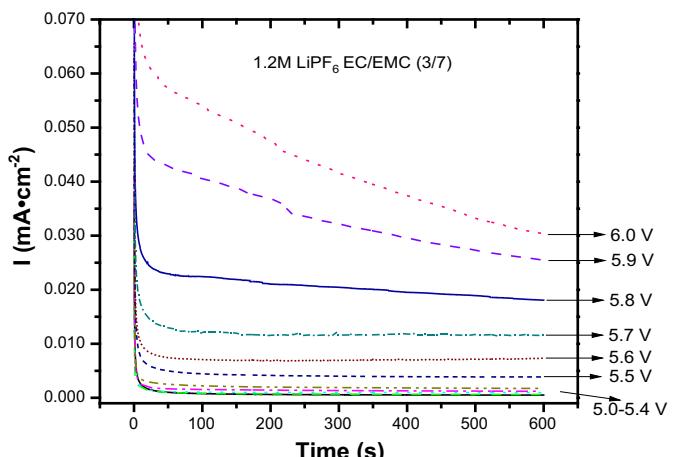


Fig. 1. Anodic stability of Gen 2 electrolyte at various potentials using Pt/Li/Li electrochemical cell (potential: 5.0 V–6.4 V vs. Li/Li⁺).

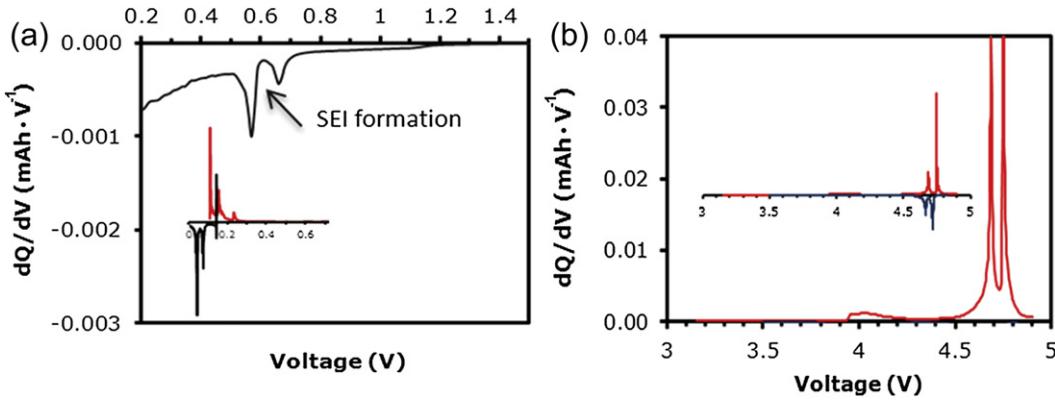


Fig. 2. (a) Differential capacity (dQ/dV) profiles of Gen 2 electrolyte in Li/graphite; (b) Li/LNMO half cells at room temperature. (Conditions: for Li/graphite cell, CC between 1.5 and 0.01 V, C/15 = 0.2 mA; for Li/LNMO cell, CC between 3.5 and 4.9 V, C/12 = 0.2 mA.)

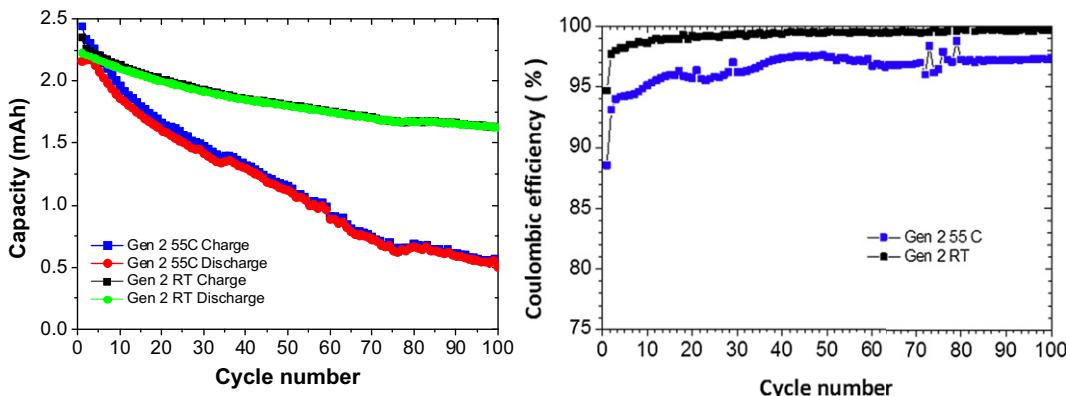


Fig. 3. Cycling profile and coulombic efficiency of Gen 2 graphite/LNMO cells at room temperature and 55 °C (Condition: CC between 3.5 and 4.9 V, C/3 = 0.67 mA, then CV at 4.9 V for 5 min or until $I \leq 0.067$ mA, C/30.)

5 min or until the charging current fell below 0.067 mA (C/30). The very obvious difference between the cycling profile at room temperature (RT) and 55 °C demonstrates that the decomposition of Gen 2 electrolyte is much more severe at elevated temperature. The capacity retention of the Gen 2 full cell is around 75% at RT, whereas the capacity retention at 55 °C is only around 25%. The coulombic efficiencies reflect the same trend. At RT the coulombic efficiency quickly reaches 99% over a few cycles and stays above 99.5% for most of the remaining cycles. In comparison, the coulombic efficiency at 55 °C remains below 98% for the entire duration of 100 cycles, suggesting that severe electrochemical decomposition occurs in the cell.

The degradation of the Gen 2 electrolyte performance in the graphite/LNMO full cell is also accompanied by rapid overpotential buildup caused by the increased impedance and polarization as the electrolyte continuously decomposes. Fig. 4 shows the voltage profile of the cell at 55 °C. The charging overpotential built up at a very fast rate, rising about 0.2 V over 50 cycles. When the cell reached the 100th cycle, the charging plateau almost disappeared, raising the question of proper setting of the cut-off potential. In lower voltage systems, the cut-off potential is usually set at a value below 4.3 V. In this case it does not matter if the cut-off potential is raised by 0.1 V or 0.2 V because such change will not lead to electrolyte decomposition. As a result, the charging will not terminate prematurely, and the cell can always complete the charging plateau. However, in the case of the high voltage cell, even raising the cut off potential by 0.1 V may lead to much more severe decomposition, making completion of charging at later cycles more

difficult. The trade-off between letting the cell complete its charging plateau and the risk of more severe electrolyte decomposition makes increasing the cut-off potential a dilemma for the Gen 2 electrolyte.

3.3. Effect of cut-off potential

To demonstrate the effect of raising the cut-off potential on the decomposition of the Gen 2 electrolyte, the graphite/LNMO full

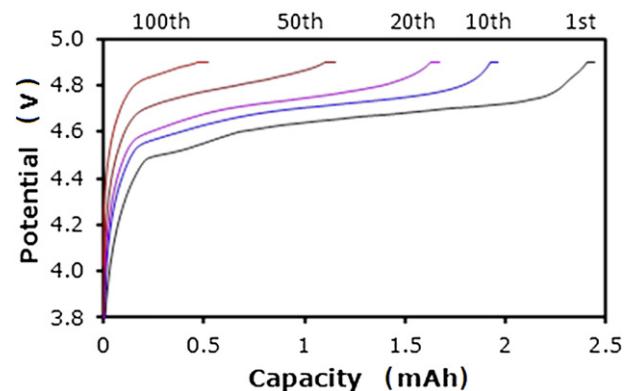


Fig. 4. Voltage profiles of Gen 2 cells at 55 °C (Condition: CC between 3.5 and 4.9 V, C/3 = 0.67 mA, then CV at 4.9 V for 5 min or until $I \leq 0.067$ mA, C/30.)

cells were tested at higher cell voltages (4.9–5.3 V), shown in Fig. 5. From the cycling profile shown in Fig. 5a, it seems that raising the cut-off potential from 4.9 V to 5.1 V does not have an extensively negative effect on the cycle performance. However, the low coulombic efficiency (Fig. 5b) of the 5.1 V cut-off potential apparently shows more severe decomposition under this condition. When the cut-off potential was further increased to 5.3 V, the capacity dropped significantly at the beginning cycles, and the coulombic efficiency remained below 80% for the whole 100 cycles. When more carefully examining the voltage profile of the first formation cycle of the 5.3 V experiment, a new plateau appears just slightly below 5.3 V in the charging process, probably corresponding to the massive electrochemical decomposition of the Gen 2 electrolyte. This plateau disappeared after the first cycle probably due to raised overpotential of the cell (Fig. 6).

3.4. Effect of constant voltage charging

The degree of completion of the charging process can be improved not only by raising the cut-off potential, but also by using a constant-voltage (CV) charging step at the end of the constant-current charging. Since raising the cut-off potential is not a viable option, we introduced a CV charging step at 4.9 V with a cut-off current set at 0.1 mA (C/20) without the 5-min limit. Under this condition the cell is charged at 4.9 V continuously until the current passing through the cell falls below 0.1 mA. The result of this experiment at 55 °C is shown in Fig. 7. Both the cycling profile and the coulombic efficiency profile show that Gen 2 electrolyte suffers from CV charging. This result suggests that Gen 2 electrolyte already has considerable degree of decomposition at 4.9 V; thus, maintaining the cell voltage at 4.9 V for longer time causes the cell performance to deteriorate faster. If a CV current limit of 0.05 mA (C/40) is used, the charging of the cell will never end due to the leakage current of electrolyte which is larger than 0.05 mA.

3.5. Optimized charging condition for Gen 2 electrolyte

Based on the previous cycling experiments, raising the cut-off potential or introducing CV charging at 4.9 V both has a negative effect on the cycle performance. This is actually a very understandable phenomenon observed in other Li-ion battery systems as well [12]. People usually tend to overcharge batteries slightly to get the full capacity out of the battery. However, in the high voltage lithium ion battery where the electrolytes experience extensive decomposition at the upper charging limit, it is very risky to further increase the charging limit potential or let the cell remain at high

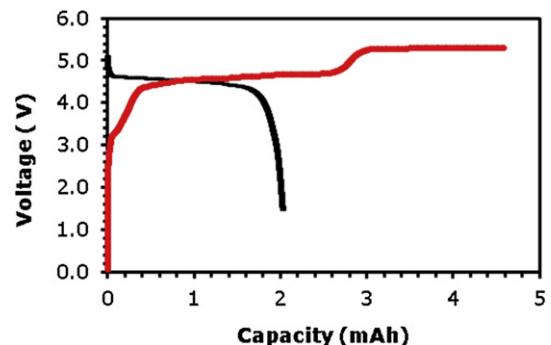


Fig. 6. Charge and discharge voltage profile of formation cycle of Gen 2 cell at room temperature. (Condition: CC between 3.5 and 5.3 V, C/3 = 0.67 mA.)

potential for prolonged time. Contradictory to this way of leading to rapid capacity fade, incomplete charge because of too little exposure at high voltage potential can also lead to faster capacity fade as well. In an effort to reduce the decomposition yet still maximize the degree of charging, we tried cycling the Gen 2 graphite/LNMO full cell from 3.5 V to 4.8 V while adding a CV charging step without time limit at the end of the constant-current charging, hoping that this combination may result in better cell performance. The cut-off current is also set at 0.1 mA (C/20). Fig. 8 shows the result of this experiment. At both RT and 55 °C, the cycling profiles show much better capacity retention for the 4.8 V experiments than the corresponding 4.9 V experiments. However, the initial capacities are lower for the 4.8 V than the 4.9 V experiments, despite the fact that the same electrodes were used. This phenomenon suggests that despite introduction of the CV charging step, reducing the cut-off potential to 4.8 V lowered the degree of completion of the charging process, thus resulting in the reduced initial capacity. However, reducing the cut-off potential to 4.8 V does alleviate electrolyte decomposition. We concluded that at 4.9 V, Gen 2 electrolyte starts to experience massive decomposition, while the graphite/LNMO system also needs to be charged to 4.9 V to properly realize its theoretical capacity. This dilemma makes Gen 2 a poor choice for the graphite/LNMO system.

3.6. Electrolyte decomposition mechanism on LNMO electrode

Regardless of the conclusion mentioned above, it is worthwhile to investigate whether Gen 2 electrolyte decomposes on the anode or cathode surface or both for the sake of future improvement.

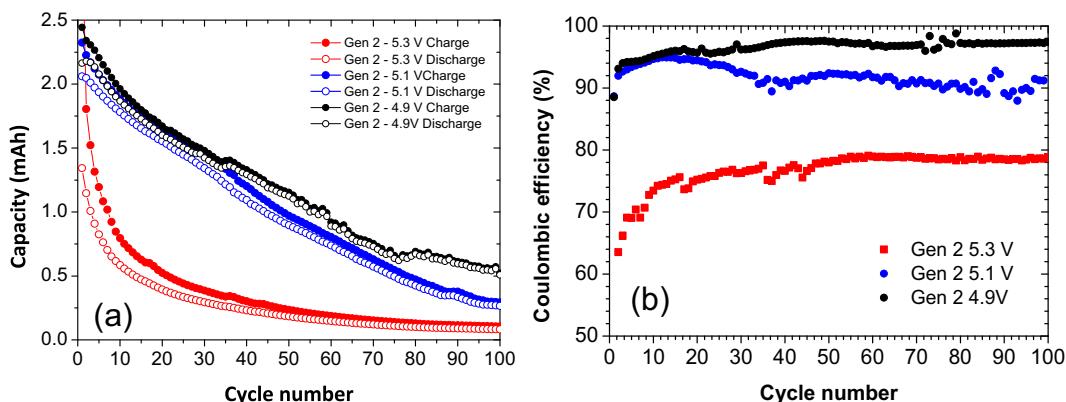


Fig. 5. (a) Cycling profile of Gen 2 cells at 55 °C with cut-off potential at 4.9 V, 5.1 V, and 5.3 V; (b) Coulombic efficiency. (Condition: CC between 3.5 and designated potential, C/3 = 0.67 mA, then CV at designated potential for 5 min or until $I \leq 0.067$ mA, C/30.)

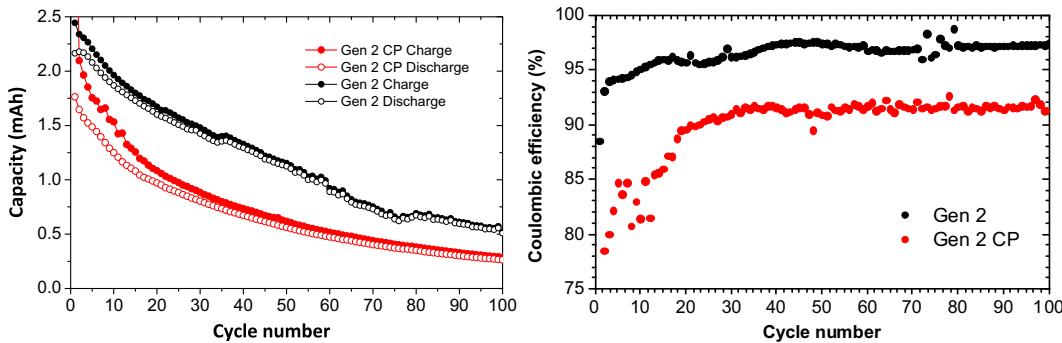


Fig. 7. Cycling profile and coulombic efficiency of Gen 2 cells with and without an unlimited-time constant voltage charging step at 55 °C (For limited-time CV charging condition: CC between 3.5 and 4.9 V, C/3 = 0.67 mA, then CV at 4.9 V for 5 min or until $I \leq 0.067$ mA, C/30. For unlimited-time CV charging condition: CC between 3.5 and 4.9 V, C/3 = 0.67 mA, then CV at 4.9 V until $I \leq 0.1$ mA, C/20.)

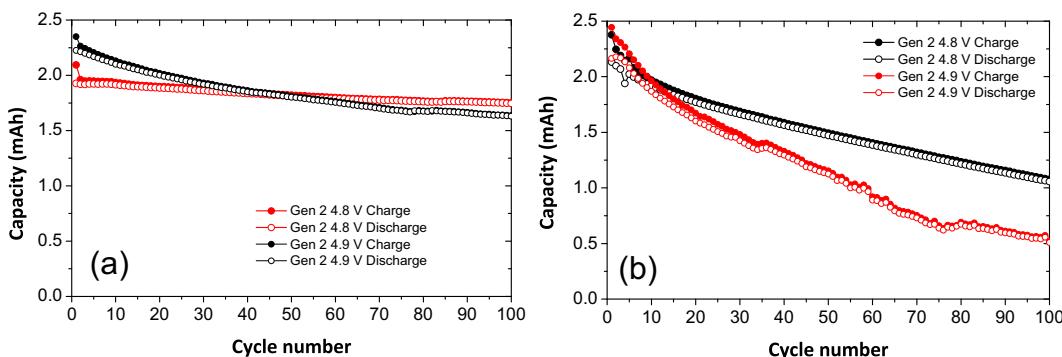


Fig. 8. (a) Capacity retention of Gen 2 cells with cut-off potential at 4.8 V and 4.9 at room temperature; (b) at 55 °C (For 4.9 V condition: CC between 3.5 and 4.9 V, C/3 = 0.67 mA, then CV at 4.9 V for 5 min or until $I \leq 0.067$ mA, C/30. For 4.8 V condition: CC between 3.5 and 4.8 V, C/3 = 0.67 mA, then CV at 4.8 V until $I \leq 0.1$ mA, C/20.)

Although the decomposition is expected to occur on the cathode side, it could happen on the anode side as well, especially at high temperature. To test this possibility, the Li/LNMO and Li/graphite half cells were cycled at 55 °C. The results are shown in Fig. 9. The cycling profile suggests that Gen 2 electrolyte decomposes on both the cathode and the anode surface, characterized by the sharp decline of the capacity on the cycling curve. However, half cells are more complex than the full cell due to the use of lithium metal as the anode. On the one hand, the cyclability of lithium metal, especially at high temperature, is questionable due to problems such as dendrite formation. On the other hand, the excess lithium metal from the counter electrode may provide compensation to the active lithium materials lost due to decomposition and SEI formation. As a result, these half cell experiments may show

sudden decline of cell performance, as well as capacity retention plateaus that were not observed in the full cell experiments. For the Li/LNMO half cell, the very long plateau from the 1st to 40th cycle seems to suggest the electrolyte is stable on the cathode surface. However, the low coulombic efficiency at the plateau stage implies that decomposition still occurs. The near 100% capacity retention at this stage is almost certainly due to lithium compensation from the lithium metal anode. In contrast, although the Li/graphite half cell has a much shorter plateau, the high coulombic efficiency at this stage suggests much less electrochemical decomposition than in the Li/LNMO half cell. The sudden decline of the cell performance may result from several factors. The 40-cycle plateau with the Li/LNMO cell suggests that the lithium metal anode should not have as extensive a problem as the

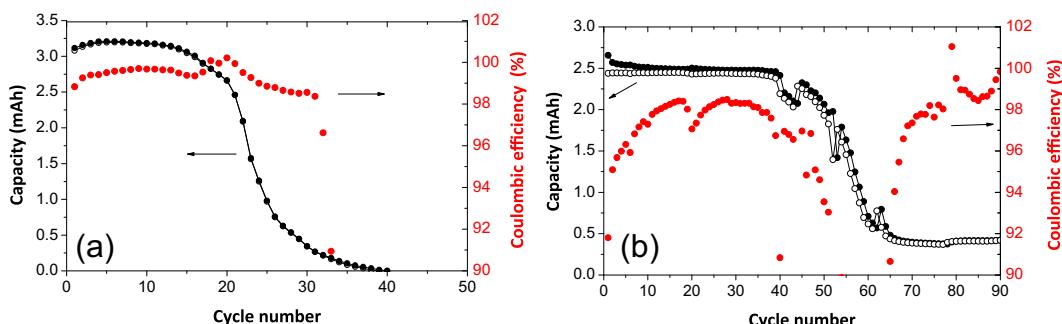


Fig. 9. (a) Cycling profile and coulombic efficiency of Gen 2 in Li/graphite cell; (b) in Li/LNMO cell. (Conditions for Li/graphite cell: CC between 1.5 and 0.01 V, C/3 = 1.0 mA. Conditions for Li/LNMO cell: CC between 3.5 and 4.95 V, C/2.5 = 1.0 mA.)

Li/graphite half cell. However, since in the graphite/LNMO full cell no sudden decline of the cell capacity was observed, such phenomenon may have some connection with the cyclability of the lithium metal. As a result, the degradation of the lithium metal may play a role in the cell sudden decline, but other factors must have contributed as well. It has been reported that the SEI formed by EC-based electrolytes are not stable at elevated temperature [13], so SEI corruption may also play an important role in this observation in the Li/graphite cell.

4. Conclusions

The stability and charging condition for the EC/EMC-based Gen 2 electrolyte have been investigated at both room temperature and elevated temperature via a series of tests using graphite/LNMO full cells and Li/graphite and Li/LNMO half cells. It was found that for the high-voltage graphite/LNMO cell, Gen 2 electrolyte decomposes readily above 4.9 V, and such decomposition becomes much more severe when the temperature is increased to 55 °C or when the cell is charged to even higher voltage. The cell performance is optimal in terms of capacity retention when charged to 4.8 V, followed by a constant potential charging step, at the cost of lowered degree of charge. The coincidence that the decomposition potential of Gen 2 electrolyte and the end of charging plateau of the graphite/LNMO electrode couple are both around 4.8–4.9 V makes optimizing the charging condition problematic. The half cell study suggests that the decomposition of Gen 2 electrolyte is most severe on the cathode side, while at elevated temperature the graphite electrode has SEI stability problems. In conclusion, the EC/EMC-based electrolyte is a poor choice for the high-voltage graphite/LNMO system. To enable use of this electrolyte in high voltage/high temperature systems, cathode additives that protect the electrolyte from oxidative decomposition as well as anode SEI

additives that can form a high-temperature-stable SEI layer on graphite are both needed. We are also actively looking into other solutions, such as solvents that tolerate higher oxidation potential than 5.0 V vs. Li/Li⁺.

Acknowledgments

This research is supported by U.S. Department of Energy, Vehicle Technologies Office. We would like to thank the Cell Fabrication Facility of Argonne Chemical Science and Engineering Division for providing the electrode materials.

References

- [1] J.M. Tarascon, M. Armand, *Nature* 414 (2001) 359–367.
- [2] M. Armand, J.M. Tarascon, *Nature* 451 (2008) 652–657.
- [3] Q. Zhong, A. Bonakdarpour, M. Zhang, Y. Gao, J.R. Dahn, *J. Electrochem. Soc.* 144 (1997) 205–213.
- [4] S. Okada, S. Sawa, M. Egashira, J. Yamaki, M. Tabuchi, H. Kageyama, T. Konishi, A. Yashino, *J. Power Sources* 97–98 (2001) 430–432.
- [5] K. Xu, *Chem. Rev.* 104 (2004) 4303.
- [6] N. Imanishi, M. Fujiyoshi, Y. Takeda, O. Yamamoto, M. Tabuchi, *Solid State Ionics* 118 (1999) 121–128.
- [7] S. Levasseur, M. Menetrier, E. Suard, C. Delmas, *Solid State Ionics* 128 (2000) 11–24.
- [8] L. Yang, B. Ravdel, B.L. Lucht, *Electrochim. Solid-State Lett.* 13 (2010) A95–A97.
- [9] A. Cresce, K. Xu, *J. Electrochem. Soc.* 158 (2011) A337–A342.
- [10] Gen 2 is the abbreviation of “2nd generation electrolyte”, which is a code name used by United States Department of Energy (DOE) in the Advanced Technology Development Program for its second generation advanced lithium ion battery system. This electrolyte is designated to be used in a system with MAG-10 synthetic graphite as anode material and LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ (NCA) as cathode material.
- [11] Z. Zhang, H. Wu, L. Hu, W. Weng, M. Koh, P. Redfern, L.A. Curtiss, K. Amine, *Energy Environ. Sci.*, in press.
- [12] M. Broussely, Ph. Biensan, F. Bonhomme, Ph. Blanchard, S. Herreyre, K. Nechev, R.J. Staniiewicz, *J. Power Sources* 148 (2005) 90–96.
- [13] A.M. Andersson, K. Edström, *J. Electrochem. Soc.* 148 (2001) A1100–A1109.